

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION
No. 24780, A.D. 1948.

Manufacture of Oxidation Products from Olefinic Compounds

We, GERARD DUNSTAN BUCKLEY, ALAN PICKLES DRIVER and FRANCIS STEPHEN BRIDSON JONES, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

10 This invention relates to the manufacture of oxidation products of olefinic compounds by means of nitrous oxide, and more particularly to the manufacture of aldehydes and ketones thereby.

15 It is known that nitrous oxide dissociates into oxygen and nitrogen at about 600° C., and can react with hydrogen at slightly lower temperatures. It is also known that oxidation of olefines by

20 known oxidising agents yields many products, but not aldehydes or ketones containing the same number of C atoms.

According to the present invention, we react nitrous oxide with one or more olefinic compounds, preferably at super-atmospheric temperature and pressure. As olefinic compounds we can use any compound containing a carbon-carbon double bond. In the case of olefinic hydrocarbons, those having a terminal double bond give aldehydes and others give ketones. The process includes the formation of olefine oxide, and can be

carried out in presence of oxidation catalysts, solvents, and diluents, if desired. 35 The process may also be carried out continuously or batchwise, and convenient temperatures and pressures are 200°—300° C. and 100—500 atmospheres.

EXAMPLE 1. 40

36 parts of cyclohexene are charged to a stirred stainless steel autoclave of capacity approximately double the liquid volume. The air remaining in the vessel is replaced by nitrous oxide, and the 45 autoclave is heated to 300° C. Additional nitrous oxide is then pumped in until the total pressure is 500 atmospheres. After stirring for 1 hour, the pressure is released and the liquid product is distilled giving 26 parts of cyclohexanone and 14 parts of unchanged cyclohexene.

EXAMPLE 2.

30 parts of propylene are treated with nitrous oxide as described in Example 1. 55 The temperature is maintained at 250° C. and the pressure at 500 atmospheres for 13 hours. After cooling and releasing the pressure, the liquid product consists substantially of propionaldehyde. 60

Dated the 22nd day of September, 1948.

E. A. BINGEN,
Solicitor for the Applicants.

PROVISIONAL
SPECIFICATION
No. 822, A.D. 1949.

Manufacture of Oxidation Products from Olefinic Ethers

We, GERARD DUNSTAN BUCKLEY, ALAN PICKLES DRIVER and FRANCIS STEPHEN BRIDSON JONES, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

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This invention relates to the manufacture of oxidation products of olefinic ethers by means of nitrous oxide, and more particularly to the manufacture of esters thereby.

It is known that nitrous oxide dissociates into oxygen and nitrogen at about 600° C., and can react with hydrogen at slightly lower temperatures. It is also

known that oxidation of olefines by known oxidising agents yields many products, but not aldehydes or ketones containing the same number of C atoms.

5 In our co-pending application 24780/48 we have described a process for making oxidation products of olefinic compounds by means of nitrous oxide.

10 According to the present invention, we react nitrous oxide with one or more olefinic ethers in which the oxygen is directly attached to a carbon atom which also has a double bond, preferably at superatmospheric temperature and pressure. As olefinic ethers we can use 2,3-dihydropyran, 2,3-dihydrofuran, vinyl ethyl ether, methyl propenyl ether, ω -methoxy styrene. The process can be carried out in presence of oxidation catalysts, solvents, and diluents, if desired. The process may also be

carried out continuously or batchwise, and convenient temperatures and pressures are 200°—300° C. and 100—500 atmospheres.

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EXAMPLE 1.

50 parts of 2,3-dihydropyran are charged to a stirred stainless steel autoclave of capacity approximately double the liquid volume. The air remaining in the vessel is replaced by nitrous oxide, and the autoclave is heated to 300° C. Additional nitrous oxide is then pumped in until the total pressure is 500 atmospheres. After stirring for 2 hours, the pressure is released and the liquid product is distilled giving 10 parts of δ -valerolactone and 40 parts of unchanged 2,3-dihydropyran.

Dated the 11th day of January, 1949.

E. A. BINGEN,
Solicitor for the Applicants.

**PROVISIONAL SPECIFICATION
No. 19509, A.D. 1949.**

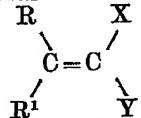
Manufacture of Cyclopropanes and Ketones from Isoolefines

40 We, GERARD DUNSTAN BUCKLEY, ALAN PICKLES DRIVER and FRANCIS STEPHEN BRIDSON JONES, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of cyclopropanes and ketones from isoolefines by means of nitrous oxide.

It is known that nitrous oxide dissociates into oxygen and nitrogen at about 600° C. and can react with hydrogen at 55 slightly lower temperatures. In our co-pending application 24780/48 we have described a process for making oxidation products of olefinic compounds by means of nitrous oxide, and exemplified the manufacture of ketones and aldehydes containing the same number of carbon atoms as the olefine used.

According to the present invention, we react nitrous oxide with one or more isoolefines of general formula



where R and R¹ are hydrocarbon or substituted hydrocarbon groups, and X and Y are hydrogen or halogen. The process is preferably carried out at superatmospheric temperature and pressure, conveniently at 200°—300° C. and 100—500 atmospheres. The process can be carried

out continuously or batchwise, and if desired in presence of oxidation catalysts, 75 solvents and diluents. The products are a cyclopropane derivative, a ketone, and nitrogen. The reaction apparently proceeds by oxygen replacing the =CXY group in one molecule of isoolefine, and 80 addition of this group at the double bond of another molecule of isoolefine. The ketone and cyclopropane derivative can be separated from the reaction mixture by fractional distillation.

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EXAMPLE 1.

A cooled high pressure reaction vessel was half-filled with 20 parts by weight of liquid isobutene. The air remaining in the vessel was replaced by nitrous oxide, 90 the temperature was then raised to 250° C. and nitrous oxide was admitted to a total pressure of 500 atm. These conditions were maintained during 2 hours, after which the reaction vessel was cooled to 95 60°—70° C. and the contents blown off through a series of traps surrounding by liquid air. The contents of the traps were then allowed to stand 12 hours in a chamber cooled to —65° C., while the bulk of 100 the nitrous oxide evaporated off. The residue was then distilled through a train of washers maintained at 45°—50° C. and containing sodium bisulphite solution and sodium carbonate solution. The gas was 105 dried by passing it over fused calcium chloride, condensed in a receiver maintained at —20° C., and distilled to give 1.5 parts (by weight) of 1,1-dimethylcyclopropane boiling at 19°—21° C.

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EXAMPLE 2.

A high pressure reaction vessel was half-filled with 30 parts (by weight) of methylenecyclohexane. The air remaining in the vessel was replaced by nitrous oxide, the temperature was raised to 300° C., and the pressure was then raised to 500 atm. by the admission of more nitrous oxide. These conditions were maintained for 4 hours, after which the reaction vessel was cooled to room temperature. The pressure in the vessel was then released, the exit gases being condensed in suitable traps surrounded by liquid air. The nitrous oxide in the traps was allowed to evaporate, and the residue was mixed with the material remaining in the reaction vessel and distilled up to a temperature of 140° C. at 25 mm. Hg. The

distillate was washed with sodium bisulphite solution and sodium carbonate solution and with water, and finally dried by standing over fused calcium chloride. The product was then distilled through an efficient column, and 5 parts by weight of 2,5-spirooctane, boiling at 125°—126° C., was collected. Cyclohexanone was recovered from the bisulphite compound by treatment with sodium carbonate. The liberated ketone was separated, dried by standing over anhydrous magnesium sulphate, and distilled. The yield was approximately 5 parts by weight of cyclohexanone boiling at 156° C.

Dated the 25th day of July, 1949.

E. A. BINGEN,
Solicitor for the Applicants.

COMPLETE SPECIFICATION**Manufacture of Oxidation Products from Olefinic Compounds**

We, GERARD RUNSTAN BUCKLEY, ALAN PICKLES DRIVER and FRANCIS STEPHEN BRIDSON JONES, all of Winnington Hall, Northwich, Cheshire, and all British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of carbonyl compounds and cyclopropanes from olefinic compounds by means of nitrous oxide at an elevated pressure, and more particularly to the manufacture of aldehydes, ketones, esters and cyclopropane derivatives.

It is known that nitrous oxide dissociates into oxygen and nitrogen at about 600° C. and can react with hydrogen at slightly lower temperatures. It is also known that at very high temperatures mixtures of certain organic compounds with relatively large proportions of nitrous oxide are combustible and yield carbon dioxide and water. It is known that olefines can be oxidised by a number of known oxidising agents, but all such reactions yield a variety of products and in general degrade the olefine so that the products contain fewer carbon atoms. For example, aldehydes and ketones can be obtained by oxidising olefines, but these products contain fewer carbon atoms than the original olefines, and therefore the reaction is not so useful as it would be if the product contained as many carbon atoms as the original olefine.

We have found that olefinic compounds

can be oxidised by heating them with a limited amount of nitrous oxide at a high pressure. After oxidation, cooling the reaction products and releasing the pressure, the reaction products can be separated from any unreacted material and from nitrogen which is formed simultaneously. Further separation may also be carried out where necessary by fractional distillation.

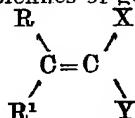
According to the present invention, therefore, we manufacture carbonyl compounds and cyclopropanes by a process which comprises contracting an olefinic compound with nitrous oxide at a temperature between 200° and 400° C. and a pressure about 20 atmospheres, cooling the mixture and releasing the pressure. In the preferred form of the process we employ not more than 2 volumes, generally not more than 1 volume, of nitrous oxide per volume of organic compound measured at the operating temperature and pressure.

In general the reactions are carried out most conveniently at a temperature between 200° and 350° C., though the actual temperature is not critical within this range. The operating pressure exceeds 20 ats. and may be even as high as 2000 ats., but advantageous results are obtained at pressures exceeding 100 ats. and there is no need to exceed 500 ats.

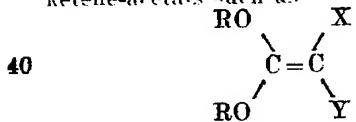
The oxidation of olefinic hydrocarbons according to the present process yields aldehydes or ketones, the aldehydes being obtained from olefines which have a terminal double bond and the ketones being obtained from these and other olefines. The aldehydes and ketones have the same number of carbon atoms as the olefines

used except in the case of isoolefines. The yield of aldehydes or ketones depends of course on the reaction conditions, and on the particular material used, but generally the conversion exceeds 50% and can be substantially complete. Any unchanged olefine can readily be separated from the product by fractional distillation.

- 10 In the particular case of isoolefines the reaction also gives rise to a cyclopropane derivative. Such cyclopropane derivatives are normally difficult to produce, and the present invention provides a 15 ready means of converting isoolefines into cyclopropane derivatives. In this case we may use isoolefines of general formula



where R and R¹ are hydrocarbon or substituted hydrocarbon groups, and X and Y are hydrogen or halogen. The reaction apparently proceeds by oxygen replacing the =CXY group in one molecule of isoolefine, and addition of this replacing group at the double bond of another molecule of isoolefine. The ketone and cyclopropane derivatives can be separated from the reaction mixture by fractional distillation after allowing the nitrogen 20 byproduct to separate. We can also use olefinic ethers in which the oxygen atom is attached to a carbon atom having a double bond. Certain of these olefinic ethers give rise to esters containing the same number of carbon atoms. e.g. 2,3-dihydropyran gives rise to δ -valerolactone, and vinyl ethers give a formic ester and a cyclopropyl ether. Similarly, ketene-acetals such as



yield carbonic esters and cyclopropane derivatives.

We believe that the oxidation process proceeds by the formation of an addition compound wherein nitrous oxide is added at the double bond giving a 5-membered ring containing two adjacent carbon atoms, two adjacent nitrogen atoms and an oxygen atom. The exact method of addition may well differ with different olefinic compounds, and clearly effects the nature of the product.

The process can be carried out in the presence of oxidation catalysts though there is no necessity to do so. Solvents and diluents however are sometimes useful especially where it may be desirable

to have present a relatively inert material, such as a saturated hydrocarbon, in order to avoid explosive decomposition. In particular, basic solvents such as tertiary organic bases like dimethylaniline and pyridine accelerate the reaction. In general the amount of the solvent should be as much as or more than the amount of unsaturated compound.

The process may be carried out batch-wise by stirring a suitable mixture in a pressure vessel and heating it. After completion of the reaction, which may take from a few minutes to a few hours depending on the reaction conditions, the pressure vessel is cooled and the pressure released. The subsequent separation of the product or products depends naturally upon what is being made, but in general this is carried out by fractional distillation.

In addition to the substances used in the examples, we can use ethylene, 1-butene, 2-butene, tetramethylethylene, 4-propyl-3-heptene, 1-dodecene, 2-methylbutene-1, 1-chloropropene-1, 1-chloroisobutene, cyclopentene, 1-methylcyclopentene, 1-phenylecyclohexene, α -methylstyrene, ω -methoxy styrene, allyl ether, methallyl alcohol, 4-vinylcyclohexene, allene, allyl chloride, ketene dimethyl acetal, phenylketene diethyl acetal, vinyl methyl ether, vinyl ethyl ether, divinyl ether, methyl propenyl ether, dimethylallyl, 2:4-hexadiene, methyl oleate, ethyl undecylenate, 2:3-dihydrofuran, 1:2-dihydrofuran, N-vinylphthalimide, vinyl butyl sulphide, vinyl phenyl sulphide, cyclooctene, cyclooctatetraene and hexatriene.

The process can also be carried out continuously by passing a suitable mixture through a heated vessel and cooling the issuing products and fractionating them as before. In the latter case the proportions are preferably 1 part of nitrous oxide by volume to 1 part of unsaturated compound or unsaturated compound plus diluent measured at the reaction temperature and pressure.

The invention is illustrated but not restricted by the following examples.

EXAMPLE 1.

36 parts of cyclohexene are charged to a stirred stainless steel autoclave of capacity approximately double the liquid volume. The air remaining in the vessel is replaced by nitrous oxide, and the autoclave is heated to 300° C. Additional nitrous oxide is then pumped in until the total pressure is 500 atmospheres. After stirring for 1 hour, the pressure is released and the liquid product is distilled giving 26 parts of cyclohexanone and 14 parts of unchanged cyclohexene.

EXAMPLE 2.

30 parts of propylene are treated with nitrous oxide as described in Example 1. The temperature is maintained at 250° C. and the pressure at 500 atmospheres for 1½ hours. After cooling and releasing the pressure, the liquid product consists substantially of propionaldehyde.

EXAMPLE 3.

10 A cooled high pressure reaction vessel is half-filled with 20 parts by weight of liquid isobutene. The air remaining in the vessel is replaced by nitrous oxide, the temperature is then raised to 250° C. 15 and nitrous oxide is admitted to a total pressure of 500 atmospheres. These conditions are maintained during 2 hours, after which the reaction vessel is cooled to 60°—70° C. and the contents blown off 20 through a series of traps surrounded by liquid air. The contents of the traps are then allowed to stand for 12 hours in a chamber cooled to —65° C., while the bulk of the nitrous oxide evaporates off. 25 The residue is then distilled through a train of washers maintained at 45°—50° C. and containing sodium bisulphite solution and sodium carbonate solution. The gas is dried by passing it over fused 30 calcium chloride, condensed in a receiver maintained at —20° C., and distilled to give 1.5 parts (by weight) of 1,1-dimethylcyclopropane boiling at 19°—21° C.

EXAMPLE 4.

35 A high pressure reaction vessel is half-filled with 30 parts (by weight) of methylenecyclohexane. The air remaining in the vessel is replaced by nitrous oxide, 40 the temperature is raised to 300° C., and the pressure is then raised to 500 atmospheres by the admission of more nitrous oxide. These conditions are maintained for 4 hours, after which the reaction 45 vessel is cooled to room temperature. The pressure in the vessel is then released, the exit gases being condensed in suitable traps surrounded by liquid air. The nitrous oxide in the traps is allowed to 50 evaporate, and the residue is mixed with the material remaining in the reaction vessel and distilled up to a temperature of 140° C. at 25 mm. Hg. The distillate is washed with sodium bisulphite solution 55 and sodium carbonate solution and with water, and finally dried by standing over fused calcium chloride. The product is then distilled through an efficient column, and 5 parts by weight of 2,5-spirooctane, 60 boiling at 125°—126° C., is collected. Cyclohexanone is recovered from the bisulphite compound by treatment with sodium carbonate. The liberated ketone is separated, dried by standing over

anhydrous magnesium sulphate, and distilled. The yield is approximately 5 parts by weight of cyclohexanone boiling at 156° C.

EXAMPLE 5.

50 parts of 2,3-dihydropyran are charged to a stirred stainless steel autoclave of capacity approximately double the liquid volume. The air remaining in the vessel is replaced by nitrous oxide, and the autoclave is heated to 300° C. 75 Additional nitrous oxide is then pumped in until the total pressure is 500 atmospheres. After stirring for 2 hours, the pressure is released and the liquid product is distilled giving 10 parts of δ-valerolactone and 40 parts of unchanged 2,3-dihydropyran.

EXAMPLE 6.

A silver-lined stirred autoclave is half filled with 40 parts of 1-chloro-1-propene and the remaining air is swept out with nitrous oxide. The temperature is raised to 280° and nitrous oxide is compressed in to a pressure of 500 atmospheres. The vessel is stirred under these condition for 90 4 hours. After cooling and releasing the pressure, the liquid product is fractionally distilled. There is thus obtained 10 parts of monochloracetone and 30 parts of unchanged 1-chloro-1-propene.

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EXAMPLE 7.

45 parts of 2:4:4-trimethylpentene-1 are treated with nitrous oxide at 300° C. and 100 500 atmospheres pressure for 4 hours by the method of Example 1. The product consists of a mixture of equal parts of 4:4-dimethyl-pentan-2-one and 1-methyl-1-neopentylcyclopropane, which may be separated by fractional distillation.

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EXAMPLE 8.

45 parts of 2:4:4-trimethylpentene-2 are treated with nitrous oxide at 275° C. and 110 400 atmospheres pressure for 4 hours by the method of Example 1. Fractional distillation of the product yields 7 parts of 2:4:4-trimethylpentan-3-one of boiling point 136°—137° C.

Use of 45 parts of 2:5-dimethyl-2:4-hexadiene instead of the trimethylpentene 115 results in the production of 9 parts of isopropyl isobutetyl ketone of boiling point 154°—155° C.

EXAMPLE 9.

45 parts of vinyl n-butyl ether are 120 treated with nitrous oxide at 300° C. and 550 atmospheres pressure for 4 hours by the method of Example 1. Fractional distillation of the product yields 25 parts of unchanged vinyl n-butyl ether, 10 125 parts of n-butyl formate and 15 parts of an azeotrope containing 30% of n-butyl

acetate and 70% of cyclopropyl *n*-butyl ether

EXAMPLE 10.

5 parts of 1:1-bis-*p*-methoxyphenyl ethylene dissolved in 40 parts of light petroleum (b.p. 60°—80° C.) are treated with nitrous oxide at 250° C. and 500 atmospheres pressure for 8 hours by the method of Example 1. After cooling and releasing the pressure, the solid product consisting of 2.5 parts of *pp'*-dimethoxybenzophenone is filtered off. Evaporation of the filtrate leaves 2.5 parts of crude 1:1-bis-*p*-methoxyphenylecyclopropane, which may be further purified by crystallisation from methanol.

EXAMPLE 11.

A solution of 5 parts of acenaphthylene in 40 parts of cyclohexane is treated with nitrous oxide at 300° C. and 500 atmospheres pressure for 5 hours by the method of Example 1. After cooling and releasing the pressure, the solution is filtered and the cyclohexane is removed by distillation. There then remain 3 parts by acenaphthenone of melting point 118° C.

EXAMPLE 12.

A mixture of 20 parts of cyclohexene and 20 parts of dimethylaniline is treated with nitrous oxide at 220° C. and 500 atmospheres pressure for 2 hours by the method of Example 1. Fractional distillation of the product yields 10 parts of cyclohexanone.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of carbonyl compounds and cyclopropanes which comprises contacting an olefinic compound with nitrous oxide at a temperature between 200° and 400° C. and a pressure above 20 atmospheres, cooling

the mixture, and releasing the pressure.

2. Process for the manufacture of aldehyde and/or ketones, in which an olefinic hydrocarbon is contacted with nitrous oxide as claimed in Claim 1.

3. Process for the manufacture of cyclopropanes and ketones, in which an isoolefine is contacted with nitrous oxide as claimed in Claim 1.

4. Process for the manufacture of esters, in which an olefinic ether wherein the oxygen atom is attached to a doubly-bound carbon atom, is contacted with nitrous oxide as claimed in Claim 1.

5. Process for the manufacture of esters and cyclopropane ethers in which a vinyl ether is contacted with nitrous oxide as claimed in Claim 1.

6. Process for the manufacture of esters and cyclopropane derivatives in which a ketene acetal is contacted with nitrous oxide as claimed in Claim 1.

7. Process as claimed in any of the preceding claims carried out at a temperature between 200° and 350° C. and a pressure exceeding 100 atmospheres.

8. Process as claimed in any of the preceding claims in which the products are separated by fractional distillation.

9. Process as claimed in any of the preceding claims in which the quantity of nitrous oxide is not more than 2 volumes, preferably not more than 1 volume, per volume of organic compound, measured at the operating temperature and pressure.

10. Process for the manufacture of oxidation products of olefinic compounds substantially as hereinbefore described with reference to each of the foregoing examples.

11. Aldehydes, ketones, cyclopropane derivatives and esters whenever obtained by the process of any of the preceding claims.

Dated the 21st day of September, 1949.

E. A. BINGEN,

Solicitor for the Applicants.

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